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On The
Reaction of Certain Alcohols
with
Para-Diazo-Meta-Toluene-Sulphonic Acid.

-Dissertation-

Presented for the Degree
of
Doctor of Philosophy

at the
Johns Hopkins University

by
W. V. Metcalf.
1890.

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Whatever of value is contained in the following dissertation is due to Professor Remsen of this University, at whose suggestion and under whose guidance the work was performed.

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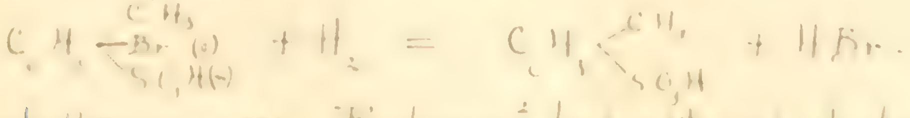
[illegible] [illegible]
[illegible] of the [illegible] [illegible]
[illegible] of results [illegible]

Introduction

The following thesis is an account of an investigation in reference to the action of methyl, ethyl and propyl alcohols on para-diazo meta-toluene sulphonic acid.

Since this work, it was necessary to prepare a considerable amount of meta-toluene sulphonamide. Several methods of making the compound were on record, two of which were adapted to preparing it in quantity. In 1873, J. C. G. Müller[1] had obtained it, by reducing the barium salt of ortho brom meta toluene-sulphonic acid by sodium amalgam, and treating the product with phosphorus pentachloride and ammonia.



$$C_6H_3\begin{cases}CH_3\\Br\ (o)\\SO_3H\ (m)\end{cases} + H_2 = C_6H_4\begin{cases}CH_3\\SO_3H\end{cases} + HBr.$$

The following year Fichmann[2] had obtained it by boiling para diazo meta toluene sulphonic acid with alcohol under a pressure of 200 m.m. of mercury, and treating the product with phosphorus pentachloride and ammonium hydrate.

$$C_6H_3\begin{cases}CH_3\\SO_3\ (m)\\N_2\ (p)\end{cases} + C_2H_5OH = C_6H_4\begin{cases}CH_3\\SO_3H\end{cases} + C_2H_4O + N_2$$

It was observed, however, that the products obtained

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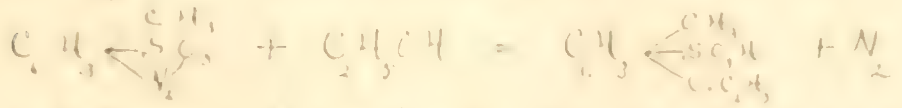
[1] Ann. Chem. Pharm. 171: 193

[2] Ann. Chem. Pharm. 169: 19

by the different processes were not identical. The difference lay, principally, in the melting points of the amides, and in the solubility and modes of crystallization of the salts of the corresponding sulphonic acids.

It was thought that, probably, the discrepancies were due, in part at least, to the fact that the reaction did not take place wholly as Remsen supposed, that there was formed also a certain amount of the ethoxy-amide which remained mixed with the meta-toluene-sulphonamide, as an impurity. The reaction in this case would be

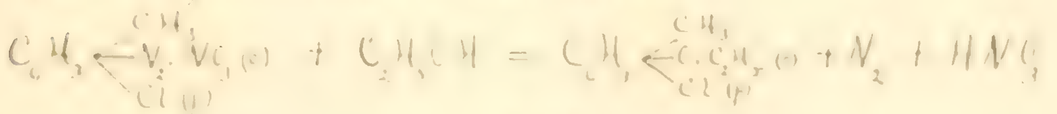


$$C_6H_3\begin{cases}CH_3\\SO_2\\N_2\end{cases} + C_2H_5OH = C_6H_3\begin{cases}CH_3\\SO_2NH_2\\O.C_2H_5\end{cases} + N_2.$$

It was determined to investigate this hypothesis by a careful study of the action of alcohol on the diazo compound in question.

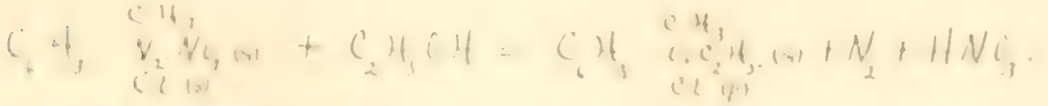
It will be remembered that Griess, in his famous work on the diazo compounds, gives as one of the important reactions, the transformation which these compounds undergo with alcohol. He found, in a number of cases, that when diazo compounds were boiled with absolute alcohol,

the diazo group was replaced by hydrogen, the alcohol being reduced to aldehyde and nitrogen being set free. This has been called, for convenience, the hydrogen reaction. He concluded that it was a general reaction for all the diazo compounds, and his conclusion remained for some time unchallenged. In 1870, however, E. Wroblewsky[1] found that, when the diazo compounds from the two isomeric chlortoluidines were boiled with absolute alcohol, the following reactions took place:



$$C_6H_3 \begin{matrix} CH_3 \\ N_2.NO_3\ (o) \\ Cl\ (p) \end{matrix} + C_2H_5OH = C_6H_3 \begin{matrix} CH_3 \\ O.C_2H_5\ (o) \\ Cl\ (p) \end{matrix} + N_2 + HNO_3$$

and



$$C_6H_3 \begin{matrix} CH_3 \\ N_2.NO_3\ (m) \\ Cl\ (o) \end{matrix} + C_2H_5OH = C_6H_3 \begin{matrix} CH_3 \\ O.C_2H_5\ (m) \\ Cl\ (p) \end{matrix} + N_2 + HNO_3.$$

This has been called the ether reaction.

Since that time, about thirty cases have been brought to light in which diazo compounds give this rather than the hydrogen reaction with alcohol. A complete list of the cases recorded up to the year 1889 will be found in W. R. Orndorff's ~~dissertation~~ Thesis on the diazo-alcohol reaction. The cases described in the following dissertation are

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[1] Ber. 3: 98

investigation of the action of the alcohols upon paradiazo meta toluene sulphonic acid.

The starting point in the investigation was the ordinary crystalline para-toluidine.

Preparation of para-toluidine-meta-sulphonic acid.

The para-toluidine-meta sulphonic acid was made from para-toluidine according to the method of Pechmann[1]. To 100 grm. of para-toluidine were added 200 grm. of fuming sulphuric acid. Thereupon the mass heated, turned dark, and gave off fumes of sulphur dioxide. [It was found afterward that the yield was somewhat better if the para-toluidine was added gradually to the fuming sulphuric acid, with frequent stirring, thus preventing the temperature from rising too high.] The mixture was then kept at a temperature of 180° for about an hour. The heating should be stopped and the mass allowed to cool, as soon as the odor of the sulphur dioxide fumes [illegible] the brown mass. Pechmann's work has shown that, if the heating is continued beyond this point, the comparative yield of para-toluidine meta-sulphonic acid

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[1] Ann Chem Pharm 173. 195

and of the disulphonic acid is much increased. After cooling, the material was poured into twice its volume of water; the mixed sulphonic acids crystallized on standing, giving a dark grey, semi-liquid pasty mass. The liquid was drained off from this mass as completely as possible with a filter pump, and, afterwards, by heavy pressure between the plates of a screw-press. The liquid thus obtained, was very dark, almost black. On standing for two or three weeks, there crystallized out from it a considerable quantity of long thin plates, apparently belonging to the triclinic system. These were purified by boiling with animal charcoal and recrystallization. By this treatment they were obtained in a pure-white condition, but were not examined further. In all probability, they were crystals of the para toluene disulphonic acid mentioned by [illegible]. The dark mass, that remained after pressing the liquid out, consisted principally of the meta- and ortho sulphonic acids of toluene. It was placed in a large evaporating dish, and the remaining sulphuric acid precipitated by an excess of barium hydroxide solution. The solution was then boiled

barely for some time to drive off any toluene that might have remained unacted upon by the sulphuric acid. (As a rule, this was found unnecessary, but occasionally there remained quite an excess of unchanged toluene.) The excess of barium was then precipitated as accurately as possible with sulphuric acid, the barium sulphate filtered off, and the filtrate evaporated to crystallization. It was found that considerable quantities of the sulphonic acids were precipitated with the barium sulphate. It was, therefore, necessary to boil the precipitate several times with water, filter, and add the wash water to the original filtrate, in order to avoid serious loss of material. This is especially true when the solution is too concentrated. It is best to work with a large amount of water—from 8 to 10 liters for every 100 grms of the original toluene. The solution, freed from barium and sulphuric acid, (a slight excess of sulphuric acid does no harm), was evaporated until it began to crystallize and then allowed to cool. On cooling, long, beautiful, in prismatic needles of the meta acid crystallized out, seeming to fill the whole

long. The appearance is very deceptive, as the crystals shrink to a small bulk when filtered. They were filtered off, and the mother liquor evaporated nearly to dryness, and allowed to crystallize. A considerable quantity of the monosymmetric crystals of the ortho acid were obtained from the mother liquor, and also from the first crystallization of the meta acid. The two acids may be separated either by the difference in the solubility of the lead salts, or of the potassium salts, or by crystallizing the acids themselves from dilute alcohol[1]. The latter method was found more convenient and satisfactory, involving less loss of material.

If the crystals of the meta-acid are small (which result may be obtained by crystallizing rapidly with stirring), an almost complete separation may be secured through the difference in the specific gravity of the two acids. The mixed acids were shaken up with a considerable quantity of dilute alcohol (say fifty per cent), and, after partial settling, the lighter crystals of the ortho acid were poured off. By repeated shaking and settling and pouring away and [illegible] [illegible]

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[1] Am. Chem. Journ. 17, 99. Am. Chem. Journ. [illegible]

used in practical diazotating) the two acids may be obtained in a nearly pure condition. The separation is completed by a single crystallization from dilute alcohol in which the ortho acid is but very slightly soluble. The meta acid still retains a yellow color which it is difficult to remove. It may be obtained, however, in a pure white condition by repeated boiling with animal charcoal and recrystallization.

Preparation of para-diazo meta-toluene sulphonic acid

Pechmann[1] recommends diazotizing the meta acid, by suspending either in alcohol or water, and treating with nitrous acid. Later, it was shown, however, that, on account of the solubility of the diazo compound in water, it is preferable to use alcohol.

Notwithstanding this, water was used as the medium, in the first experiments tried. It was first cooled, and a rapid stream of nitrous fumes passed through it. The reaction took place very rapidly. Some twenty grams of the acid were diazotized in less than ten minutes. The product obtained was a compound [illegible], nearly white. The yield, however,

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[1] Ann. Chem. Pharm. 173. 201

was very poor, less than fifty percent of theoretical. A large proportion of the diazo compound remained in solution in the water, necessitating its being got out [illegible] separately.

In all subsequent experiments, ninety five percent of alcohol was used (say 250 c.c. to 25 gm of the acid), and was found to work very satisfactorily. The alcohol, in which the finely ground acid was suspended, was placed in an Erlenmeyer flask. On passing the nitrous fumes through it, it gradually heats, turning yellow, and finally a bright yellowish red. The yellow acid then changes rapidly over to the pink, or pinkish-white, product of the diazo-compound. The whole process requires about thirty minutes. While the alcohol remains cold, little or no action takes place. By the action of the nitrous fumes, the material is heated only by passing upwards, but time is saved by heating the alcohol to 30°–40° before beginning the reaction. The temperature should not be allowed to rise above 40°, otherwise there is danger of considerable decomposition. The temperature may be easily regulated when there is danger of too great heat, by placing the flask

in a bath of cold water. The higher the temperature at which the action takes place, the darker is the pink color of the resulting diazo-compound. By careful treatment, especially if absolute alcohol is used, the product may be obtained in a very nearly pure white condition. The action is hastened by continual shaking. When the action is complete, the diazo-compound is ~~then~~ filtered by means of a filter-pump, washed with alcohol and then with a little ether. The yield is very good, or eighty five to ninety five per cent of theoretical. Sometimes gas, if the acid may be continuously energetic at one time. The diazo-compound, if perfectly dry and kept in the dark, remains unchanged for a long time; if kept in a moist condition it rapidly turns yellow. Even the dry compound gradually decomposes when exposed to the light, though it may be kept for several days without undergoing any change.

It is interesting to note in passing that the ortho-sulphonic acid of paratoluidine is more easily diazotized than the corresponding ortho-acid both in water and in alcohol. In several of the diazotizing experiments that were tried, the

meta-acid which contained a small amount of ortho acid as an impurity. In these cases, there remained invariably a residue of the ortho-acid, after all the meta-acid had passed over into the diazo compound. The same fact was observed when water was used as the medium, in which the acid was suspended. To test this point more carefully, two grams of the acid were ground up together with ninety two percent of alcohol added to the mixture, nitrous fumes were passed through it for about thirty minutes. There they remained a considerable residue of the unchanged ortho acid, while all of the meta acid had been converted into the diazo compound. The mixture was shaken rapidly during the course of the diazotizing process to prevent any separation of the two acids by the difference in their specific gravity.

The experiments show that the meta acid is more easily diazotized than the ortho acid.

Apparatus for heating water under pressure.

The para-diazo-meta-toluene sulphonic acid, obtained by the method described above, was used in the study

of the [illegible] reaction. In this case, it was necessary to heat the liquid employed under [illegible] pressure. The apparatus employed for this purpose was the same as that used by [illegible] in their work on the [illegible] [illegible] [illegible] It consists of the following parts: —— A strong litre boiling flask (A), covered with a close net work of copper wire (about [illegible] inch mesh) to prevent danger from flying glass, in case the flask should burst. This is fitted with a two-hole, rubber stopper, which is bound down by wire during the experiment. Into one of the holes of this stopper is fitted a bent glass tube (B), connecting with a U tube (C), which contains mercury. This tube (C) is graduated in millimeters and is used as a manometer. Into the other hole of the rubber stopper is fitted a curved, copper tube having in its upper end a conical valve (D), pressed down by a lever and weight (E), as shown in the figure. [See next page]

When the liquid in A is boiled, the pressure of the vapor gradually increases until it is just sufficient to raise the

conical valve allowing the vapor
to escape. During the
heating the pressure remained
very constant and this pressure
it may be regulated by
adjusting the position of
the weight (L)

Action of ethyl alcohol on para diazo-meta-toluene sulphonic acid

Twenty five grams of the diazo-compound were boiled with 100 c.c. of alcohol (ninety eight percent) under a pressure of 1 gram 250 mm of mercury. At first there appeared to be no change, but soon the alcohol began to turn yellow. Then gradually it changed through orange-color to a deep red. The originally orange compound meanwhile [illegible]

forming a [illegible] solution. During the boiling there was a slight [illegible] of nitrogen. The reaction is completed when the diazo compound is entirely dissolved. This took place in about twenty five minutes, but the boiling was continued for some time.

In a subsequent experiment, 20 grm of the diazo compound was boiled with 300 c.c. of alcohol (ninety eight percent), under 760 mm pressure. The solution seemed to be complete in [illegible] minutes, but the boiling was continued for half an hour. In this experiment also there was only a slight [illegible] of nitrogen.

The dark red liquid obtained in this way was strongly acid in its reaction. It was poured into an evaporating dish, heated to boiling on a water bath, and neutralized as nearly as possible with dry sodium carbonate. The neutral, or slightly alkaline, solution was then evaporated to dryness on a water bath, and finally powdered and dried in an air bath. It was found in the experiments that, if any water was added with the solution, the

process of drying was an exceedingly tedious one. On evaporating, it formed a dark brown gummy mass, from which it was very difficult to drive off all the water. If, however, all the water was carefully excluded, the strong alcoholic solution evaporated and dried rapidly [illegible] dry. The resulting salt formed a brown powder. This was finely pulverized and ground together in an evaporating dish with somewhat more than an equal weight of phosphorus pentachloride. The mass gradually heated to a high temperature, foaming and giving off phosphorus oxychloride fumes. After the reaction there remained a red oil. This was washed in a large amount of cold water and treated with concentrated ammonia solution, in the usual way, to form the amide. On adding ammonia, the substance [illegible] assumed a bright yellow color and gradually became solid. The color did not disappear on standing. After the completion of the reaction, the ammonia was evaporated on a water bath and there remained a [illegible]

red, gummy, non-crystallized mass. This was washed repeatedly with a large amount of cold water until nearly all was dissolved. There remained undissolved a small amount of a dark brown, heavy substance. The water, with the substance in solution, was filtered and allowed to cool, when there crystallized out a considerable quantity of yellowish needles mixed with more or less gummy material. This was boiled with animal charcoal, and re-crystallized five times, and, thus, the substance was obtained in the form of pure white needles, with a constant melting-point of 137°-138°.

The ortho-sulphon-amide-toluene, obtained by Fahlberg, crystallizes in rhombohedral scales and melts "somewhat below 100°." The compound is moderately soluble in boiling water but very slightly so in cold water. It dissolves easily in cold alcohol, ether, and acetone but benzene dissolves it sparingly. Analysis showed the composition to be $C_7H_9SO_2N$. The results obtained were as follows:

.22391 grm. of the substance gave .2269 grm barium sulphate. This gave for the percent of sulphur 14.77. The determination was made by Liebig's method. (Two determinations were made by Carius' method, which gave [illegible] percent too low. (The determinations in this laboratory, by Carius's method, of certain especially decomposable sulphur amides, have given similar results.)

.25700 grm. of the substance gave ammonia, equivalent to 11.66 c.c. of a standard ammonia solution, containing 1.4012 grm of nitrogen to the litre.

.24822 grm. of the substance gave .45472 grm of carbon dioxide, and .1341 grm. of water.

For $C_9H_{13}O_3NS$

		Theory.	Found.
C_9	108	50.23	49.96
H_{13}	13	6.05	6.00
O_3	48	22.33	
N	14	6.51	6.35
S	32	14.88	14.77
	215	100.00	

The compound formed was undoubtedly para ethoxy meta sulphonamido toluene — $C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_2NH_2(m) \\ OC_2H_5(p) \end{smallmatrix}$

The reactions were as follows:

I. $C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_3(m) \\ N_2(p) \end{smallmatrix} + C_2H_5OH = C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_3H(m) \\ OC_2H_5(p) \end{smallmatrix} + N_2$

II. $2\,C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_3H(m) \\ OC_2H_5(p) \end{smallmatrix} + Na_2CO_3 = 2\,C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_3Na(m) \\ OC_2H_5(p) \end{smallmatrix} + CO_2 + H_2O$

III. $2\,C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_3Na(m) \\ OC_2H_5(p) \end{smallmatrix} + PCl_5 = 2\,C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_2Cl(m) \\ OC_2H_5(p) \end{smallmatrix} + POCl_3 + NaCl$

IV. $C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_2Cl(m) \\ OC_2H_5(p) \end{smallmatrix} + NH_4OH = C_6H_3 \lessdot \begin{smallmatrix} CH_3 \\ SO_2NH_2(m) \\ OC_2H_5(p) \end{smallmatrix} + HCl + H_2O$

This is one of some thirty cases, in which a diazo compound heated with alcohol, gives a substance in which the diazo group is replaced by the ethoxy group, instead of by hydrogen. The yield of the ethoxy compound was poor, by the Remsen analysis there was obtained only a little over [illegible] per cent of theoretical. The other yields were very considerably larger. These have been further examined in the corresponding naphthylamine [illegible] [illegible] [illegible] [illegible]

yield of the ethoxy compound suggests, of course, that most of the diazo compound was acted upon in the regular way, giving the reaction.

$$C_6H_3 < ^{SO_2NH_2}_{N_2HSO_4} + C_2H_5OH = C_6H_3 \overset{CH_3}{—} SO_2NH_2 + C_2H_4O + N_2$$

The absence of any strong odour of aldehyde, during the reaction, renders it improbable that the meta toluene sulphonic amide was produced to any considerable extent. To determine this point accurately, all the mother liquors, of the different crystallizations of the ethoxy compound, were worked over with great care. There was obtained, in this way, a small quantity of a mixture, made up evidently of the small rhombic scales of meta toluene sulphonic amide, together with more or less of the pure ethoxy-derivative of the same. With the small quantity at hand, it was found impossible, by repeated crystallizations to separate the two compounds completely. Possibly, with larger quantities, this might be effected more easily. The different crystallizations made in the effort to purify the meta compound, [illegible] melting between the points [illegible]

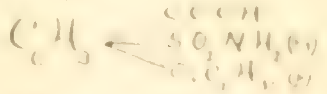
Usually the mixtures had no sharp melting-point, but melted through several degrees. A few mixtures were obtained, however, that seemed to have a fairly definite melting-point. One, for example, melted quite sharply at 105°, and recrystallization of a small amount of water in a test tube produced little change. By recrystallizing in a large amount of water, however, and filtering off the very first part of the material that crystallized out, a small quantity of the ortho-derivative was obtained in a nearly pure condition.

The experiments prove, beyond question, that the two amides crystallize together in mixtures that are exceedingly difficult to separate, and which might easily be mistaken for approximately pure substances. It is highly probable that this fact furnishes an explanation of the hitherto unexplained discrepancies between the meta-toluene sulphonic acid made from the diazo-compound, and that made, according to Müller, by the reduction of ortho-brom-meta-sulphonamido-toluene. The sulphonamide which [illegible] obtained

from the benzo-compound, had no definite melting point. [illegible] speaks of it as melting "somewhat below 110°." It was probably a mixture of the two amides.

Preparation of para ethoxy-meta-sulphon amide-benzoic acid

Having on hand a small quantity of the para-ethoxy meta toluene sulphon-amide obtained in the above experiments, it was determined to oxidize this by potassium permanganate in alkaline solution. The expectation was that the methyl would be oxidized to the carboxyl group, giving a substituted carbonic acid of the formula



$$C_6H_3 \begin{cases} COOH \\ SO_2NH_2(3) \\ OC_2H_5(4) \end{cases}$$

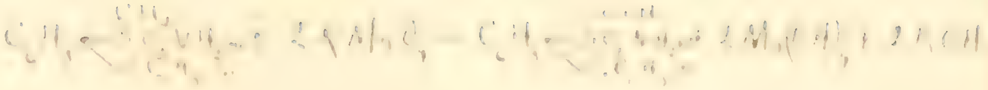
Five grams of the ethoxy amide were placed in a flask together with 170 c.c. of water and 1.8 grm of caustic potash, and heated in a water bath until the amide was entirely dissolved. There was then added a hot solution of 8 grm of potassium permanganate in 170 c.c of water. The whole was heated in a water bath until the color disappeared leaving a yellow liquid above the dark brown deposit of manganese compound

this, on cooling, deposited a considerable quantity of the unchanged amide. More potassium permanganate was therefore added, and the heating was continued until decolorization took place. The manganese hydroxide was then filtered off, and the liquid allowed to cool. After filtering to remove the small amount of unchanged amide which crystallized out, the solution was acidified with hydrochloric acid. This gave a copious precipitate of fine white needles. In order to remove the small amount of the original amide which was contained in the precipitate, it was first dissolved in hot, dilute sodium carbonate, and the solution evaporated to dryness. The dried mass was treated with a small amount of cold water, the solution filtered and the filtrate acidified. The pure white needles obtained in this way were recrystallized from water. They were almost insoluble in cold and difficultly soluble in boiling water. The solution gave a strongly acid reaction. Two and a half grams of the substance was obtained in long, beautiful needles, which seemed to be perfectly pure. It melted at

220° – 230°, with gradual decomposition as shown by the brown color which deepened as the temperature rose. To remove this colored impurity, the whole was converted into the barium salt by neutralizing the boiling solution with pure barium carbonate. The filtrate was evaporated to dryness, and thus the barium salt was obtained in the form of fine, pure white needles, only moderately soluble in cold water, and but very slightly soluble in hot absolute alcohol. The salt was boiled in absolute alcohol, to remove the last traces of the original amines, and then recrystallized once from water. After determining the water and barium in this salt it was dissolved, and the acid again precipitated with hydrochloric acid. It was then washed thoroughly and recrystallized again from water. A determination was made of the nitrogen in the acid so obtained. The analyses gave, for the barium salt, the formula — $C_{17}H_{22}O_{10}N_2SBa.2H_2O$; and, for the acid, the formula — $C_7H_{11}O_3NS$.

The reactions were as follows: —

I



$$C_6H_3\begin{cases}CH_3\\SO_2NH_2\\OC_2H_5\end{cases} + 2KMnO_4 = C_6H_3\begin{cases}COOK\\SO_2NH_2\\OC_2H_5\end{cases} + 2MnO(OH)_2 + 2KOH$$

II

$$2C_6H_3\begin{cases}COOK\\SO_2NH_2\\OC_2H_5\end{cases} + BaCl_2 + 2H_2O = \left(C_6H_3\begin{cases}COO\\SO_2NH_2\\OC_2H_5\end{cases}\right)_2 Ba.2H_2O + 2KCl$$

Analysis of barium salt

.1661 grm of the salt gave .00899 grm of water (at 210°), and .0588 grm of barium sulphate. This gives, per water, 5.41 percent — theory, 5.45 percent; and for barium, 20.80 percent — theory, 20.70 percent.

For $C_{18}H_{20}O_{10}N_2S_2Ba\,2H_2O$.

	Theory	Found
H_2O	5.45	5.41
Ba	20.70	20.80

Analysis of the acid

.2077 grm of the acid gave NH_3, equivalent to 8.447 c.c. of a standard ammonia solution, containing 1.4052 grm of nitrogen to the litre. This gives for nitrogen 5.63 percent — theory, 5.71

The acid contains no water of crystallization.

These analyses prove the essential purity of the acid, but the melting-point was still, by no means sharp. The material melted mainly at 230°–231°. It showed signs of melting, however, at 225°. The melting substance had a brown color, indicating partial decomposition.

Fusion of para-ethoxy-meta-sulphonamido-benzoic acid with caustic potash.

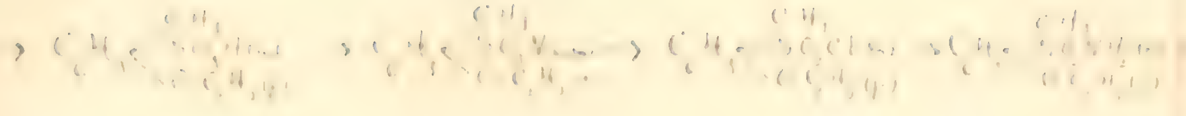
In order to confirm the proof of the constitution of the acid just described, the substance was fused with caustic potash. If the constitution given above be the true one, the ethoxy and the sulphonamido groups should be replaced by hydroxyl groups, giving the well known proto-catechuic acid.

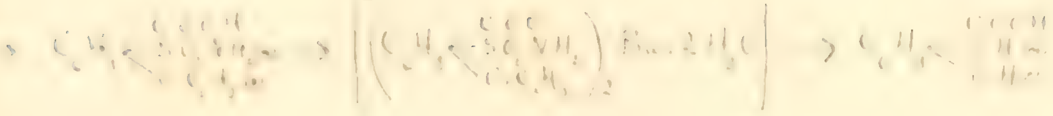
About twenty five grams of caustic potash was fused in a silver crucible, with a few c.c. of water, and one gram of the acid added to the melting mass. To determine when the action had taken place, a small quantity of the material was taken out, from time to time, on a silver spatula, and treated with acid. As soon as this treatment

gas in a place free of sulphur fumes. The mass was allowed to cool. It was then dissolved in water, and acidified with hydrochloric acid. After cooling thoroughly, the solution was shaken with ether, and the water drawn off from the ether solution by a separating funnel. The ether was then distilled, and there remained an impure, brown colored crystalline substance. This was dissolved in boiling water, giving a dark brown solution. This solution, boiled with animal charcoal, became perfectly colorless, and, on cooling, deposited crystals of proto-catechuic acid. This acid was not purified, but was simply identified by its color reactions, and its melting-point, 195° - 196° instead of 198° 199°.

Here then, we get back to a well-known substance whose constitution is thoroughly understood. We have passed from paratoluidine to proto-catechuic acid by the following steps :—

$C_6H_4<^{CH_3}_{NH_2(p)} \rightarrow C_6H_3<^{CH_3}_{SO_3H(m)}_{NH_2(p)} \rightarrow C_6H_3<^{CH_3}_{SO_3H(m)}_{N_2(p)} \rightarrow$





Action of methyl alcohol

on para-diazo-meta-toluene-sulphonic acid.

The study of the action of ethyl alcohol on para-diazo-meta-toluene-sulphonic acid naturally suggested the question whether methyl alcohol would act in the same way. The question was tested, and the results obtained were, in general, analogous to those obtained in the case of ethyl alcohol. The reaction was found to work more perfectly, however, with the methyl alcohol.

15 grm of the diazo compound was heated with methyl alcohol for fifty minutes, under a pressure of 450 degrees. The temperature of the alcohol boiling at this pressure, was 58°. Under ordinary pressure it would boil over, boiling the liquid 65 - 66°.

As the diazo compound dissolved the color changed from

pounds, resembling in appearance the corresponding liquid dissolved in ethyl alcohol. The solution was heated nearly to boiling in an evaporating dish, and then neutralized with dry sodium carbonate. The sodium salt so formed was difficultly soluble in methyl alcohol. It was precipitated so copiously that the whole became semi-solid, even before neutralization was complete. The salt was then partially dried on the water bath, and finally pulverized and the drying completed in an air bath at 110°.
If all water be carefully excluded, the whole process of drying requires less than an hour. The salt contained

[illegible]

Preparation of pure methoxy-ortho-toluene sulphon chloride

Treated with an equal weight of phosphorus pentachloride, and washed with cold water, the sodium salt gave a clear heavy oil, much lighter colored, however, than the corresponding ethyl compound. The oil solidified, on cooling, to a white crystalline mass. By repeated recrystallization from commercial ligroin,

It yields a pure crystalline substance of a faint yellow or brown color. Long boiling with animal charcoal, and repeated crystallization, failed to remove the color. It melts sharply at 194°. It is nearly insoluble in cold ether and ligroine. In boiling benzene, it dissolves readily, and is deposited again, almost completely, as the solution cools. Benzene, therefore, seems the best solvent from which to recrystallize it. In boiling water it dissolves slowly, with decomposition. When crystallized rapidly from a concentrated solution, it comes down in the form of fine needles. By spontaneous evaporation from benzene, it crystallized in aggregations of large orthorhombic plates. By spontaneous evaporation of a long narrow column of the ether solution, larger crystals were obtained showing a greater variety of forms. The following planes were observed: base plane, prism, macropyramid, brachypyramid, macrodome, brachydome and perhaps the pyramid. The crystals were shown to belong to the orthorhombic system by the interference figures and the parallel

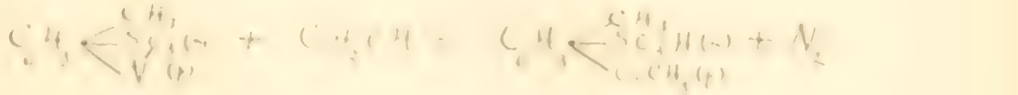
[illegible]

Analysis: Chlorine determination revealed the following formula $C_8H_9O_3SCl$

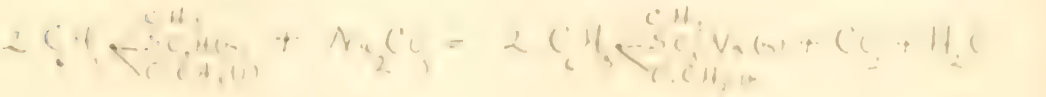
[illegible] gram of the chloride gave [illegible] gram of silver chloride. This gave Chlorine 16.01 per cent, theory 16.06 per cent.

This analysis was confirmed, as will be described later, by analysis of the corresponding amide, and of various salts of the corresponding acid.

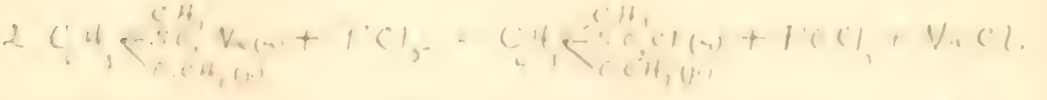
The reactions which took place are as follows.

I 

$$C_6H_3 \begin{cases} CH_3 \\ SO_3 \, (o) \\ N \, (p) \end{cases} + CH_3OH = C_6H_3 \begin{cases} CH_3 \\ SO_3H \, (o) \\ O.CH_3 \, (p) \end{cases} + N_2$$

II 

$$2\, C_6H_3 \begin{cases} CH_3 \\ SO_3H \, (o) \\ O.CH_3 \, (p) \end{cases} + Na_2CO_3 = 2\, C_6H_3 \begin{cases} CH_3 \\ SO_3Na \, (o) \\ O.CH_3 \, (p) \end{cases} + CO_2 + H_2O$$

III 

$$2\, C_6H_3 \begin{cases} CH_3 \\ SO_3Na \, (o) \\ O.CH_3 \, (p) \end{cases} + PCl_5 = C_6H_3 \begin{cases} CH_3 \\ SO_2Cl \, (o) \\ O.CH_3 \, (p) \end{cases} + POCl_3 + NaCl.$$

The best yield that was obtained was a little less than forty per cent of theoretical.

By working over the benzene mother liquors, a small amount of a second was obtained, insoluble in cold water, soluble with decomposition in boiling

water, forming a solution with which silver nitrate gives a copious precipitate of silver chloride. This oil was not examined with care, but was in all probability the ortho sulphon chloride of toluene. The corresponding amide was formed by treating the oil with concentrated ammonia, but the quantity was so small that it was impossible to identify it clearly. It was probably formed according to the ordinary reactions as follows:—

I $C_6H_3 \overset{CH_3}{\underset{N_2}{<}} SO_3 + CH_3OH = C_6H_4 \overset{CH_3}{<} SO_3H + CH_2O + N_2.$

II $2\ C_6H_4 \overset{CH_3}{<} SO_3H + Na_2CO_3 = 2\ C_6H_4 \overset{CH_3}{<} SO_3Na + CO_2 + H_2O.$

III $C_6H_4 \overset{CH_3}{<} SO_3Na + PCl_5 = C_6H_4 \overset{CH_3}{<} SO_2Cl + POCl_3 + NaCl.$

It is evident that the reaction takes place to some extent in connection with the methoxy reaction as will be shown later, in connection with the amide.

Preparation of pure methoxy-metatoluene sulphonic acid

In order to obtain the acid corresponding to the

methenyl sulphonyl chloride, 100 grams of the purified chloride was boiled with about one liter of distilled water for an hour and a half. (a balloon flask, with an inverted condenser, being used to prevent loss.) At the end of this time, the solution was nearly complete, there remaining only a slight impurity suspended in the fluid. The solution, when filtered, was colorless. On evaporating it became somewhat brown, and yielded long, prismatic needles, quite easily soluble in water. These were dissolved, boiled with animal charcoal, and filtered. In this way, a perfectly colorless solution was obtained, but on evaporation, it again turned brown, yielding a crystalline substance which still had a yellowish color. The melting point also indicated that the substance was impure. The solution contained a small amount of sulphuric acid which must have come from the decomposition of the acid. It was found, however, that this acid, when dissolved in water, and purified with

animal charcoal, yielded pure salts with the carbonates of barium and lead.

In order to obtain a pure specimen of the acid, one-third gramme of the pure lead salt was used. (See below.) This was dissolved in water and the lead precipitated from the solution by hydrogen sulphide. The perfectly colorless solution left, after filtering off the lead sulphide, was evaporated over a water bath. The solution turned dark as it approached crystallization, and gave a brown product. Another portion of the lead salt was then prepared, and precipitated by hydrogen sulphide, and the colorless solution thus obtained, was evaporated on a water bath until it began to have a faint yellowish tinge. It was then allowed to evaporate spontaneously in a vacuum. After four or five days, the evaporation was complete, and the acid obtained as a nearly pure substance. It also had a yellowish brown color, however. Undoubtedly the perfectly pure acid is white.

The acid melted at [illegible]. It apparently loses some water on evaporating over a water bath. It was not analyzed, as its composition was sufficiently plain from the mode of formation and the analysis of its salts.

Preparation of barium salt

Two and one half grams of the acid was dissolved in water, and the boiling solution was neutralized with barium carbonate. The solution was then filtered and evaporated to dryness, and then a white salt was obtained which crystallized in needles. The barium salt thus obtained is exceedingly soluble in water; slightly, if at all, soluble in cold alcohol or ether. It is moderately soluble in boiling alcohol. Barium determinations gave the following results:—

I. .2[illegible] grm. of the salt gave .120[illegible] grm. of barium sulphate.

II. [illegible] grm. of the salt gave [illegible] grm. of barium sulphate.

Cal. for Ba$\left(C_6H_3\begin{matrix}CH_3\\SO_3\\CH_3\end{matrix}\right)_2$

	Theory	Found	Average
Ba =	23.87	23.81 , 23.77	23.79

The specimen analyzed was obtained by evaporating the solution to dryness on a water bath. So prepared, it contained no water of crystallization. It is not unlikely that, by spontaneous evaporation of the water solution, a salt would be obtained containing water.

Calcium Salt.

To make the calcium salt, two grams of the acid were dissolved in water, and the solution neutralized by adding an excess of pure calcium carbonate. The solution was filtered, and evaporated. During the evaporation, gypsum crystallized out from the solution and was filtered off. It was then evaporated nearly to dryness, dissolved in a very small quantity of cold water, filtered, and again evaporated to dryness. In this way, a salt was obtained that crystallized in white, shining flakes

yellowish, solid. It is extremely soluble in water, apparently soluble in cold alcohol. It dissolves much more readily in boiling alcohol, but, like the barium salt, it does not crystallize easily from this medium, except by spontaneous evaporation. There seems to be a strong tendency to form a supersaturated solution, from which the salt would not separate except by evaporation. It is strongly hygroscopic. After drying on a water bath, it absorbs water rapidly, but takes up no definite amount, as was shown by several determinations. It can not be dried in a desiccator. Possibly a definite amount of water of crystallization might be shown to exist, if the salt were obtained by spontaneous evaporation, and dried between filter paper under pressure. The water was not so determined.

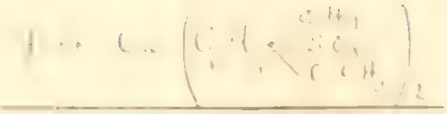
The salt was dried at 150°, and then three determinations of the calcium oxide, which gave the following results:—

.21276 grm of the salt gave .06763 grm calcium sulphate.

.19886 grm of the salt gave .04558 grm of calcium sulphate.

.21981 " " " " " .05791 " " "

"



For Ca [illegible] $_2$

Theory	Found	Average
Ca 7.63	7.53 7.52 7.58	7.56

The analyses showed that a little calcium sulphate still remained, mixed with the salt. 1.62 percent of calcium sulphate, mixed with the salt, would give the above result.

Preparation of lead salt.

The lead salt was prepared by adding pure lead carbonate to a strong, boiling solution of the acid. The solution was stirred thoroughly, after which it was filtered and concentrated. From a concentrated solution, the salt crystallized in white needles. *[It is considerably less soluble in water than the corresponding calcium and barium salts. [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]

---

* [illegible] appear on next page

The barium and calcium salts [illegible] easily [illegible] crystallize, while the barium and calcium salts are [illegible] [illegible] [illegible] [illegible]]

The salt [illegible] was obtained by crystallizing from water, was treated with boiling alcohol (78°). The product [illegible] dissolved completely, giving a clear solution, even after cooling, showing that it was free from lead sulphate. The alcoholic solution was evaporated to dryness, and the product again recrystallized from water.

So obtained, it gave the following analyses for water and lead:

.4996 gm. of salt, gave off, at 160°, .0118 gm. of water
.5552 " " " " " " " .01432 " " "
.3851 " " " " .0819[illegible] gm. of lead sulphate
.3041 " " " " .09505 " " "

$$\text{[illegible]}\ Pb\left(C_6H_4\overset{CH_3}{SO_3}\right)_2 . 3H_2O$$

	Theory	Found	Average
H_2O	[illegible]	[illegible] [illegible]	[illegible]
Pb	[illegible]	[illegible] [illegible]	[illegible]

The third salt studied is [illegible] salt, and this burns brilliantly, without melting, leaving a residue of carbon which finally burns completely, leaving only a black ring on the platinum. An attempt was made to determine the melting point, but it was found that decomposition begins considerably before the temperature of melting was reached. The decomposition begins at about 240°, and the melting is complete at about 260°.

An attempt was made to make the silver salt, by dissolving silver oxide in a hot solution of the acid. The salt is soluble in the [illegible] but decomposes on boiling, or concentration, [illegible] both, [illegible] depositing silver again. It was therefore not obtained in a pure condition. It was, however, [illegible] like the other salts [illegible] its solubility in water and alcohol.

The sodium salt, though not prepared, was shown to resemble the other salts, is probably [illegible] in [illegible]

Preparation of para-[illegible] sulphonic amide.

The amide was made by treating the crude chloride (obtained by the action of phosphorus pentachloride on the sodium salt), with concentrated ammonia, and evaporating to dryness. The crude amide, thus obtained, was dissolved in alcohol (92 percent), and the solution boiled with animal charcoal, filtered, and evaporated to dryness. The second crystallization from water gave pure white needles, melting at 180-181°.

In one experiment, 10.5 grm of the crude compound was boiled under a pressure of 450 mm of mercury with 100 c.c. of methyl alcohol (boiling at 65°-66°). The yield of pure amide was 4.9 grm, or about 36 percent of theoretical. The amide is but very slightly soluble in cold water, and dissolves with difficulty in boiling water. Approximate determinations showed that a liter of water at 18°, dissolves about .3 grm of the amide. A liter of boiling water dissolves about 1.6 grm. The amide is appreciably soluble in cold

alcohol was [illegible]

The following analyses show the composition of the [illegible] to be C_9H_{11} [illegible]

[illegible]

[illegible] copper oxide [illegible] 1.4 [illegible] nitrogen by the [illegible]

.2054 grm of the [illegible] gave .25465 grm of barium [illegible]

.2065 grm of the same gave .3006 grm of barium sulphate.

.2410 grm of the same gave .4230 grm of carbon dioxide and [illegible] of water.

for C_6H_4 [illegible]

		Theory	Found
C_9	[illegible]	[illegible]	[illegible]
H_{11}	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	
N	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	

The sulphur determinations were made by fusing with [illegible] [illegible], as liable to give low [illegible].

From the methoxy amide, there was obtained by working over the mother liquors, a small quantity of a product with the sulphonamide odour. It melted partially at 75 - 100°. It contained the small characteristic needles with iridescent reflection, so characteristic of this compound. The yield was very small,— less than one tenth of a gram to 4.9 grms. of the methoxy amide.

The principal reaction with the oxy compound is evidently that in which the hydrogen is replaced by the methoxy-group.

Oxidation of para-methoxy-ortho-[illegible]

It will be remembered that when the corresponding ethoxy compound was oxidized with potassium permanganate, the methyl group was replaced by carboxyl, giving a monobasic acid. A similar experiment gave equally good results with the methoxy amide.

Two grams of the amide and 1.4 grams of sodium hydroxide dissolved in 215 cc. of water, was treated with 4.4 grams of potassium permanganate, dissolved in the same amount of water. The mixture was heated on the water bath about one and a half hours, when the decolorization of the potassium permanganate was complete. The solution was filtered and allowed to cool, when a little over one gram of the unchanged amide crystallized out. The solution after filtering, containing the potassium salt of the oxidation product, together with a small amount of the original amide. It was evaporated to a small bulk, and the small amount of amide, which crystallized out, was separated by filtration. The solution was then diluted to about one half a liter, and acidified with hydrochloric acid. The white crystalline precipitate that was obtained was very slightly soluble in cold water, soluble with difficulty in much boiling water. It dissolves readily in cold alcohol. The acid recrystallized from water gave a [illegible]

mass of needles which had all the appearance of a pure substance. It melts, however, with decomposition at 240°–250°. Nitrogen and sulphur determinations also showed plainly that the product was still impure. They differed 1 percent and 2 percent from the theoretical amount for $C_6H_3\left\langle\begin{array}{l}COOH\\SO_2NH_2\\C.CH_3\end{array}\right.$ They leave little doubt, however, as to the composition of the substance. The analyses, together with the method of formation, and the analogy of the corresponding ethoxy compound, practically settle the question of its constitution. This view was entirely confirmed by the preparation and analysis of the barium salt.

Preparation of barium salt

This salt, prepared by neutralizing the hot solution of the acid by barium carbonate, was quite soluble in water, but not too much so to crystallize from a concentrated solution. It crystallizes in little clusters of pure white needles. It is nearly insoluble in strong alcohol. It was purified by

mixing with alcohol (95%), filtering and washing thoroughly with hot alcohol.

Analysis showed the composition to be $\mathrm{Ba}\left(\mathrm{C_6H_3}\begin{smallmatrix}\mathrm{CO_2}\\ \mathrm{SO_2NH_2}\\ \mathrm{CH_3}\end{smallmatrix}\right)_2 3\mathrm{H_2O}$.

.3508 gram of the salt gave, at 200°, .02807 gram of water, and .1256 gram of barium sulphate.

This gives, for the percent of water, 8.02 percent; theory 8.27 percent; and for the " " " barium 21.03 " " , " 21.04 " "

	Theory.	Found
H_2O	8.27	8.02
Ba	21.04	21.03

The last molecule of water is held very tenaciously, being driven off only by long heating at high temperature. During this last extrusion, the salt was constantly kept through ... It was very difficult to get a constant weight.

The attempt was made to get the free acid by precipitating it from the barium salt with hydrochloric acid. The specimen obtained in this way was probably pure but

it still melted with decomposition at [illegible].

It will be remembered that the corresponding ethoxy acid, although pure, [illegible] in a similar way.

No further analysis was made of the acid, as the material was needed for other experiments.

An attempt was made to convert this acid into proto-catechuic acid, by fusing with caustic potash, but the experiment was unsuccessful. It is highly probable that the failure was due to a lack of the most favorable conditions. It seems quite evident, from the constitution of the compound, and from the analogy of the corresponding ethoxy compound, that this acid would yield proto-catechuic acid under the right conditions.

Reaction of the diazo-compound with propyl alcohol.

It appears, from what has been said, that when the diazo compound under consideration,

$C_6H_3\begin{cases}COOH\\ \\ N_2\end{cases}$

is boiled, under pressure, with methyl or ethyl alcohol, the principal reaction that takes place is that in which the diazo-group is replaced

by hydrogen. It was thought of interest to determine whether the analogous reaction would take place with other alcohols. [illegible] with propyl alcohol and butyl [illegible] gave similar results.

Seventy grams of the orange compound were heated with 200 cc. of propyl alcohol under a pressure of 200 - 220 mm of mercury for about thirty minutes. The orange compound was completely dissolved, giving a dark red solution, much darker than that obtained with the methyl or ethyl alcohol. The solution was [illegible] in the dry [illegible] and evaporated to dryness on a water bath. A dark, gummy mass was left, which did not harden, even after keeping it for some time on an air bath. On cooling, however, the mass became hard, and could be pulverized. To the pulverized material was added an equal weight of phosphorus pentachloride. This gave a dark brown, gummy oil. By washing and treating with concentrated ammonia in the usual way, the crude amide was obtained

group of colorless [illegible]. This was washed with water and required crystallization. Boiling with animal charcoal did not lighten the color of the alcoholic solution.

The solution was evaporated to dryness, and the residue dissolved, boiled with animal charcoal, and recrystallized from water four times. In this way, 1.1 gm. of the pure white material was obtained. The melting point was 196.5°-198°. The substance is nearly insoluble in cold water, moderately soluble in boiling water, easily soluble in alcohol. It crystallizes in needles. (It is interesting to note that every compound obtained, including amides, salts, [illegible] etc., in which the oxygen was replaced by the [illegible] group crystallized in needles.)

The following analyses show the composition of the substance to be C[illegible]H[illegible]ONS.

[illegible] gm. of the substance gave [illegible] [illegible] [illegible] Dumas [illegible] solution containing 196/2 gm of nitrogen to the liter.

.1107 gram of the sample gave [illegible] gram of barium sulphate.

.[illegible] gram of the sample gave [illegible] gram of carbon dioxide, and [illegible] of water.

Calc. for $C_{10}H_{15}O_3NS$

		Theory	Found
C_{10}	120	52.40	52.31
H_{15}	15	6.55	6.71
O_3	48	20.96	
N	14	6.11	6.01
S	32	13.97	13.71
	229	100.00	

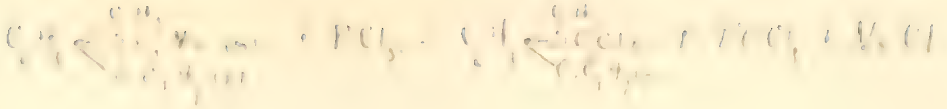
These were figured to be in favor of the determination, which gave the high result for hydrogen.

The reactions, which took place, were as follows:—

I. $C_6H_3\left<\begin{matrix}CH_3\\SO_3(4)\\N_2(1)\end{matrix}\right. + C_2H_5OH = C_6H_3\left<\begin{matrix}CH_3\\SO_3H(4)\\O.C_2H_5(1)\end{matrix}\right. + N_2$

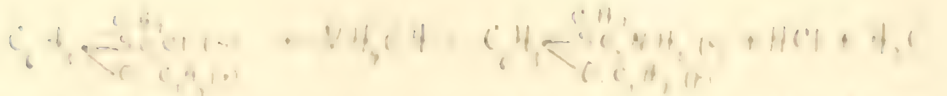
II. $2\,C_6H_3\left<\begin{matrix}CH_3\\SO_3H(4)\\OC_2H_5(1)\end{matrix}\right. + Na_2CO_3 = 2\,C_6H_3\left<\begin{matrix}CH_3\\SO_3Na(4)\\OC_2H_5(1)\end{matrix}\right. + H_2O + CO_2$

II.



$$C_6H_3\begin{cases}CH_3\\SO_3Na\ (m)\\COOC_3H_7\ (o)\end{cases} + PCl_5 = C_6H_3\begin{cases}CH_3\\SO_2Cl\ (m)\\COOC_3H_7\ (o)\end{cases} + POCl_3 + NaCl$$

III.



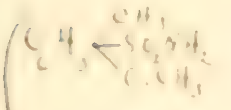
$$C_6H_3\begin{cases}CH_3\\SO_2Cl\ (m)\\COOC_3H_7\ (o)\end{cases} + NH_4OH = C_6H_3\begin{cases}CH_3\\SO_2NH_2\ (m)\\COOC_3H_7\ (o)\end{cases} + HCl + H_2O$$

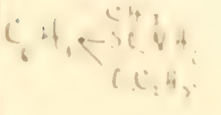
Beside this product, there was obtained from the last mother liquors, a very small quantity of a substance having a low melting point. The amount was too small to admit of purification. It did not crystallize like the remaining meta-sulphon amide toluene, but, in all probability, it contained this compound. It was doubtless produced in less quantity than the propyl compound. The yield of the latter, however, as has been seen, was ~~[illegible]~~ a very small one. 17 grams of the sodium compound giving only 1.6 gram of the pure ester amide, or about 9.8 percent of theoretical. It is to be remembered that the actual yield was several times greater than this, loss being inevitable in repeated crystallization of small amounts.

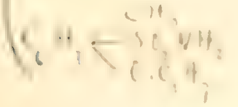
We have shown then that when the sodium compound under investigation is boiled with methyl, ethyl, or propyl alcohol, both the hydrogen and the sodium

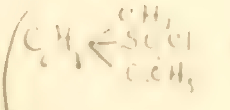
reactions take place, the relative yield of the other compound is very much greater.

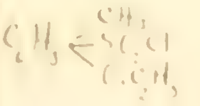
It is interesting to note in passing that the homologous compounds, however, do not obey the law which holds in the case of the simple homologous series of hydrocarbons. In each series the melting point generally increases with the complexity of the substance. The reverse is true of these compounds.

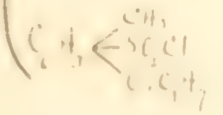

$C_6H_3 < \begin{array}{l} CH_3 \\ SO_2NH_2 \\ C.CH_3 \end{array}$ melts at 186° 187°

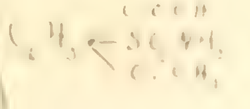

$C_6H_3 < \begin{array}{l} CH_3 \\ SO_2NH_2 \\ C.C_2H_5 \end{array}$ " " 150° 151°.

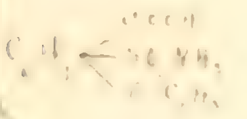

$C_6H_3 < \begin{array}{l} CH_3 \\ SO_2NH_2 \\ C.C_3H_7 \end{array}$ " " 126.5° 127°.


$C_6H_3 < \begin{array}{l} CH_3 \\ SO_2Cl \\ C.CH_3 \end{array}$ melts at 84°.


$C_6H_3 < \begin{array}{l} CH_3 \\ SO_2Cl \\ C.C_2H_5 \end{array}$ is a liquid


$C_6H_3 < \begin{array}{l} CH_3 \\ SO_2Cl \\ C.C_3H_7 \end{array}$ " " "


$C_6H_3 < \begin{array}{l} COOH \\ SO_2NH_2 \\ C.CH_3 \end{array}$ melts between 240° & 270°


$C_6H_3 < \begin{array}{l} COOH \\ SO_2NH_2 \\ C.C_2H_5 \end{array}$ " " 225° & 231°.

Pressure Experiments

The experiments described above, show that, when para-diazo-ortho-toluene sulphonic acid is decomposed with methyl, ethyl or propyl alcohol, under a pressure of 200 m.m. or more, the diazo-group is replaced by the alcoholic group to a much greater extent than by hydrogen. Some experiments were performed in order to get some insight into the question of what influence, if any, the pressure exerts on the course of the reaction. Time and material were lacking for an exhaustive study of this question, but the few preliminary experiments performed, have some value.

Three lots of the diazo-compound, of ten grams each, were taken and treated in exactly the same way, with the one exception that one was decomposed at 200, the second at 400, the third at 600 m.m pressure. The ten grams was placed in the perfectly dry pressure flask, and 250 c.c. of absolute methyl alcohol was added. The alcohol was then boiled under pressure for thirty minutes. Nitrogen was freely going off.

and the sugar was dissolved, giving a clear solution, of an orange yellow color. This was poured from the flask, without rinsing, neutralized with 4 gm of dry sodium carbonate, and evaporated to dryness on a water bath. About 11 gm of the pinkish-white sodium salt was obtained. After cooling, 11 gm of phosphorus pentachloride was added. A red oil was thus obtained, which, on cooling, solidified less perfectly than in some previous experiments. This chloride was washed in 1½ liters of cold water, each of the three lots being treated in exactly the same way. The same quantity of concentrated ammonium hydrate was then added to each. The material was allowed to stand in contact with the ammonia solution over night, and then evaporated to dryness on a water bath. The three lots of crude amide so obtained were boiled in the same quantity of distilled water. Each left a small residue of tarry matter. They were filtered through filter paper of the same

were boiled with the same amount of animal charcoal, and again filtered through the same filter.
The carbon and filter were treated with the same amount of boiling water.
On cooling, a fairly pure specimen of [illegible] amide was deposited, in each case. That which had been decomposed at 200 mm pressure, and 71° 72° temperature gave 1.195 grm of the amide, or 11.28 percent, [illegible] that decomposed at 400 mm pressure, and 75° 76° temperature, gave 1.325 grm — — , or 13.05 percent; that decomposed at 600 mm pressure, and 81° temperature, gave 1.51 grm — — , or 14.88 per cent.
The pressures were not kept perfectly constant, but varied occasionally as much as 10° each side of the number given.
The amounts obtained do not represent the entire yields, as the mother liquors were not worked over, and the animal charcoal was not boiled to dissolve out the amide clinging to it. The mother liquors and

the second [illegible] were afterward got by the [illegible] long time, in [illegible] additional quantity of the reagents [illegible]. The methyl yields [illegible] [illegible] very, though the relative yield is kept same. [illegible] the loss in each case must have been very nearly identical.

The experiments show that an increase of pressure tends to increase the yield of the methyl compound.

Some experiments, [illegible] in essentially the same way with absolutely anhydrous ethyl alcohol proved unsatisfactory. The alcohol used was [illegible], both by the method of preparation, by the specific gravity and by analysis, to be entirely pure anhydrous alcohol. The [illegible] of [illegible] was [illegible] in every one of the three experiments; and the relative yields of the [illegible] would [illegible] small, and the [illegible] is mixed with the [illegible] [illegible] [illegible] with [illegible] catalyser [illegible] at [illegible] impossible to separate it [illegible] with [illegible] [illegible]

results. The appearance of the material indicates that the lot boiled at 600 mm contained a considerably larger amount of the methoxy compound than the other.

Conditions which influence the course of the diazo alcohol reaction

The experiment, described above, together with many others¹, shows that 'Griess' reaction, for a diazo compound boiled with alcohol, is not universal. There are about one-hundred-and-fifty cases in chemical literature, in which a diazo compound has been boiled with an alcohol, and the product studied. In some thirty of these, the diazo group has been replaced by the alcoholic group, rather than by hydrogen. In several of these latter cases, however, both reactions have been shown to take place simultaneously. In fact, it is highly probable, in the light of all the evidence, that many compounds now recorded as giving the hydrogen reaction, or the ether reaction, in reality give both reactions simultaneously.

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1. Introduction

In most of the cases reported, the experiment was performed, not with the purpose of studying the reaction, but for the sake of obtaining the compound desired. The yields were, therefore, not carefully measured, and a second product might easily have been overlooked, [illegible]

It is probable that, in very many cases, the same compound yields both products simultaneously, or that the same compound yields now one product, now the other, or now an excess of the one, now an excess of the other, according to the conditions under which the reaction takes place. It is interesting, therefore, to determine the conditions which influence the course of the reaction. Some valuable work has already been done in this direction, but much more is necessary before the subject will be thoroughly cleared up. It is probable that there is no simple law governing the case, but that the results are the complex interaction of a number of causes.

Some of these may be mentioned.

I.

In 1886, Remsen & Palmer showed[1] that, when para-diazo-ortho-toluene sulphonic acid was decomposed by alcohol, both the ethoxy, and the hydrogen, reaction took place, and that the relative yield of the two products was influenced by the amount of pressure under which the experiment was performed.

They obtained the following results:

At 90 m.m. pressure, the yield of toluene sulphonic acid is greater than that of the ethoxy-compound;

At 120 m.m. pressure, the yield of the former is to that of the latter, as one is to three;

At 150 m.m. pressure, the same ratio was obtained;

At 300 m.m. pressure, the proportion of the toluene-sulphonic acid, was very small;

At 500 m.m. pressure, the ~~proportion~~ yield was almost wholly the ethoxy compound.

These figures are, of course, only approximate, but they

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[1] Am. Chem. Jour. 8:243

show that, in the instance of lead, "the higher the pressure, the larger the proportion of the ethoxy compound formed." Of course, no trustworthy generalization can be made from a single case. It is highly desirable that further study be given to the effect of pressure upon the decomposition of diazo compounds with the alcohols.

The experiments already described on the decomposition of paradiazo meta toluene sulphonic acid with methyl alcohol, indicate that, in this case, also, a low pressure is more favorable to the hydrogen reaction, while a high pressure favors the methoxy reaction.

II.

In 1889, Remsen & Orndorff[1] showed, by the study of several cases, that the presence and position of other groups in the benzene nucleus had an important influence on the course of the reaction.

This had been previously suggested by Remsen & Palmer[2], but had not been carefully worked out.

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[1] Am. Chem. Journ. 9:387 [2] Am. Chem. Journ. [illegible]

of alcohol on the nitrate and sulphate of aniline. In both these cases, contrary to Griess' work, the ethoxy compound is the chief product formed. The hydrogen reaction takes place only to a slight extent. This proves that some of the remaining free hydrogen atoms, of the benzene nucleus, must be replaced by other groups in order that the diazo-compound may give the hydrogen reaction to any considerable extent.

They next studied the action of alcohol on the diazo-compounds, formed from ortho-, meta-, and para-toluidine. The results were as follows: —

"When ortho diazo toluene sulphate is decomposed in alcohol, about 50 per cent is converted into the ethyl ether of ortho cresol", and no toluene is produced.

"When meta diazo toluene sulphate is decomposed about 40 per cent is converted into the ethyl ether of meta cresol, and no toluene is formed."

"When para diazo toluene sulphate is decomposed about 45 per cent is converted into toluene and 16 per cent

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[1] Am. Chem. Journ. 17, [illegible]

into the ethyl ether of para cresol."
The authors conclude that "the presence of a paraffin residue, in the para position, relatively to the diazo group, is favorable to the replacement of the diazo group by hydrogen."
This view is confirmed by other cases on record.
The most marked of these is furnished by [illegible][1], who showed that, when the diazo compound from nitro-toluene diamine is decomposed with alcohol, the diazo group para to the methyl, is replaced by hydrogen, while that ortho to the methyl is replaced by the ethoxy group, giving — $C_6H_3\begin{cases}CH_3 & (1)\\ O.C_2H_5 & (2)\\ NO_2 & (5)\end{cases}$ from $C_6H_2\begin{cases}CH_3 & (1)\\ NH_2 & (2)\\ NH_2 & (4)\\ NO_2 & (5)\end{cases}$.

They drew no definite conclusions as to how the nature of the substituting group affected the course of the reaction.

III

In 1886, [illegible] & [illegible][2] came to the conclusion that the nature of the substituting group, as well as its position, exerted an important influence.
They showed that the three [illegible] diazo [illegible] yield [illegible]

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[1] Ber. der deutsch. Chem. Gesell. 9, 1312. [2] Am. Chem. [illegible]

obtained, sodium employed as the only reducer. Thus that with [illegible] [illegible] nitrogen gave the hydrogen reaction, while [illegible] [illegible] gave respectively the nitrogen reaction.

These results, together with those previously given, prove clearly these propositions

$C_2H_3 \cdot N_2 \cdot [illegible]$ gives nitrogen-reaction

[illegible] hydrogen —

[illegible] — —

[illegible] — — —

[illegible] nitrogen —

[illegible] —

[illegible] — hydrogen —

In the case of the nitro- and [illegible] compounds, the nitro group causes the hydrogen reaction, while the methyl[illegible] the ~~[illegible]~~ group ~~[illegible]~~ the
[illegible]
ether reaction, which would have occurred, if no substituting group had been present.

Thus, the nitro group favors the hydrogen reaction whatever its position.

~~Acting on this suggestion, the writer made~~ a careful study of all the cases on record, in which a diazo compound has been decomposed with alcohol — the purpose being to discover, if possible, the influence of the different groups on the course of the reaction.

He considers himself justified in drawing the following conclusions.

1. The nitro group under normal conditions always produces the hydrogen reaction, whatever other groups may be present. There are but two exceptions, but neither [illegible] [illegible]

position, strong in another.

2. The sulphonic acid group favors the hydrogen reaction. Abnormal conditions, such as the presence of other groups, may readily change the tendency.

3. Bromine produces the hydrogen reaction, whatever other groups be present.

4. The methyl group, in compounds having a single benzene nucleus, favors the hydrogen reaction, only in the para position; the ethoxy reaction, only in the ortho- or meta- position. Since the influence is comparatively weak, it is suppressed by most of the other groups except chlorine.

5. Chlorine and iodine favor the hydrogen reaction; but the influence of chlorine is very weak, being suppressed by all the other groups.

6. The carboxyl group favors the hydrogen reaction in the ortho and meta positions, and the ethoxy reaction when in the para position.

the synthesis of [illegible].

7. The simplest diazo compounds with a single benzene nucleus, give the ethoxy reaction.

8. All diazo compounds, having more than one benzene ring give the hydrogen reaction.

The insignificance of the data from which these conclusions are drawn lessens materially their value. The action of the diazo compound described in the present thesis seems an exception to the rules given, although up to the present time it had been supposed to be in accordance with them. $C_6H_3 \begin{cases} \overset{N_2}{SO_3}(a) \\ CH_3(b) \end{cases}$ gives principally the ethoxy reaction, although both the sulphonic acid and the methyl groups would tend to the opposite result, according to Mr. Griffin (See rules 2 and 4). Before accurate conclusions can be reached on this line, the cases on record must be carefully reconsidered by someone who has this particular problem in mind.

The work described in the present thesis suggests two other explanations, by adding to the present,

the position in the other groups present, and their relative [illegible] changed that there has not [illegible], [illegible] are as suggestions to make of the work which is still necessary need in further work on the subject. They are as follows:

I

It seems likely that the nature of the alcohol has an influence on the reaction. The simpler the alcohol, the greater the tendency towards the alkoxy reaction. In the above experiments methyl alcohol gave about 20 percent of the theoretical yield of the methoxy compound; ethyl alcohol gave about 7 percent of theoretical for the ethoxy compound, and propyl alcohol gave about 3.5 percent of theoretical for the propoxy compound. Some experiments on Jackson showed the [illegible] [illegible] upon the alkoxy reaction with methyl, ethyl and propyl alcohol. Methyl alcohol yielded 55.56 percent of the theoretical amount, ethyl alcohol 40.52 percent, propyl alcohol [illegible] percent. From these sets of experiments suggest that the

simpler alcohol groups are introduced more easily than the more complex ones.

II

The relative yield of the ethoxy compound was invariably less with absolutely anhydrous alcohol than with 95 percent alcohol. This suggests that the presence of a small amount of water favors the ethoxy reaction.

The problem is as yet far from settled. We can say only that the results are undoubtedly due to the complex interaction of several causes. After a large number of accurate observations on the subject possibly more definite conclusions may be reached.

Summary of results

I. The accompanying scheme shows the compounds prepared and their relation to each other. Those marked * were not before described. Of these, those marked

FOLD OUT

used vigorously.

2. The presence of a slight amount of water seems to favor the alloying reaction.

These facts need further investigation.

III. It was noticed that in the homologous compounds formed the melting point becomes lower as complexity increases.

Note

I. The temperatures given above are all approximate.

II. The atomic weights used in the calculations of this thesis are as follows:—

Ag	107.7	H	1.
Ba	136.9	N	14.
C	12	O.	16
Cu	63.4	Pb	206.4
Cl.	35.4	S	32

May 20, 1890. Chemical Laboratory.

Johns Hopkins University

Biographical Sketch.

The writer of this dissertation was born in Bangor, Maine, September 2 1860. Moved to Elyria Ohio, in 1865. Prepared for college in the Elyria High School and the Preparatory School at Oberlin, Ohio. Entered Oberlin College in 1879; graduated in 1883. Studied, the two following years, at Oberlin Theological Seminary. Taught the Natural Sciences at Whitman College, Walla Walla, Washington Territory, during the years 1885 – 1887. From 1887 to date has been a student in the graduate Department of Johns Hopkins University.